# Contaminant Transport in Highly Heterogeneous Subsurface Media

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Submitted to IWW/USGS
June 2, 2008

Report Period: 02/15/07 to 02/14/08

## EXECUTIVE SUMMARY

Contaminant transport in the subsurface is a very complicated process, with researchers working on determining which processes are of the most importance when attempting to model what will happen due to the subsurface processes alone, as well as with remediation schemes in place. One of the current areas of interest includes transport through highly heterogeneous geologic materials. When contaminants move through materials which are highly heterogeneous, having a high variance in log-conductivities, the contaminant takes longer to move through the subsurface environment. It gets spread due to slower dispersion through the fine grained material vs. the course material, and is most noticeable by the 'tailing' effect seen in solute concentration vs. time data. This transport behavior is known as non-Fickian transport, which cannot be completely described by the conventional convection-dispersion equation. This research takes a simplified model of this type of environment, consisting of low-conductivity spherical inclusions inside a course, high-conductivity matrix material, and is attempting to correlate 3D laboratory and theoretical results co-currently.

Nearly 100 spherical inclusions were made in the lab from fine, low-conductivity sand. Each individual sphere was characterized, measuring its weight, volume, porosity, and hydraulic conductivity. A computer program was written to randomly generate a packing scheme for the placement of spheres within the experimental set-up (i.e. black box). Using a removable grid, the black box was wet-packed with course matrix material, with 75 fine spherical inclusions placed within the box according to the program results. It was determined that one pore volume for the box was nearly 38 Liters of water. At a flow rate of 5 ml/min, it was determined that one pore volume would take nearly 5.3 days. The box was flushed for one day with DI water, to allow the sand inside the box to settle, and then it was opened to fill any additional space that was opened up due to settling of the sand. The box was again sealed, and a pH 9 DI water solution was pumped through to

equilibrate the sand to the experimental conditions. After flushing the box for 3 pore volumes, a tracer was then injected, consisting of fluorescein and lithium bromide at pH 9. Initial results show that the experimental system does indeed result in non-Fickian tailing.

## PROJECT DESCRIPTION AND RESULTS

The objectives of this project were to (1) completely characterize the individual spheres and matrix material, (2) fill the black box with randomly placed spherical inclusions within the course silica sand matrix, (3) collect detailed information on solute transport within and at the outlet of the experimental system for multiple experimental runs, (4) create a 3D computer simulation of the laboratory system using the upscaled two-equation time-varying mass transfer model for transport in a two-region system, and (5) correlate the theoretical model to the experimental results. A summary of the results to date are included in this report, with continued research being done. Complete results will be available in the PhD thesis of Stephanie Harrington.

In attempting to more fully understand how contaminants travel with the groundwater in the subsurface environments, it is necessary to understand how heterogeneities affect flow. Some methods already exist for simplified cases, where the conductivity changes between various subsurface media are small. The case where there are two distinct media in contact which have a large variance in their respective conductivities has only recently become an area of high interest [1-11]. This highly heterogeneous type of environment has been found to cause prolonged solute transport, resulting in non-Fickian tailing. As a simplest case, this research has constructed a highly heterogeneous experimental setup consisting of a black aluminum box (100cm x 50cm x 20cm) filled with a random binary spatial conductivity field. This experimental setup is being run in order to gather a detailed set of experimental data on transport through this type of environment, with the goal of correlating the results with a new theoretical model.

Spherical inclusions were made from low conductivity silica sand by heating it in a muffle furnace in spherical molds. The resultant low conductivity (~0.01 cm/s) spherical inclusions were thoroughly characterized, measuring each one's individual weight, volume, porosity, and average hydraulic conductivity (through pressure drop measurements). Once this was accomplished, a MATLAB program was written to determine the placement of the spheres in the black box to be used for the experimental analysis. The box's internal volume was partitioned in the program, allowing for a 3D grid structure with one grid length being equivalent to 5 cm. This program allowed for a randomly generated placement for each sphere, with the stipulation that they could not be on top of or beside one another. The number of spheres placed within the box was also chosen randomly, with its stipulation being between 70 and 84 spheres total within the box. The first eligible program result determined the random placement of 75 spheres within the box (Figure 1).

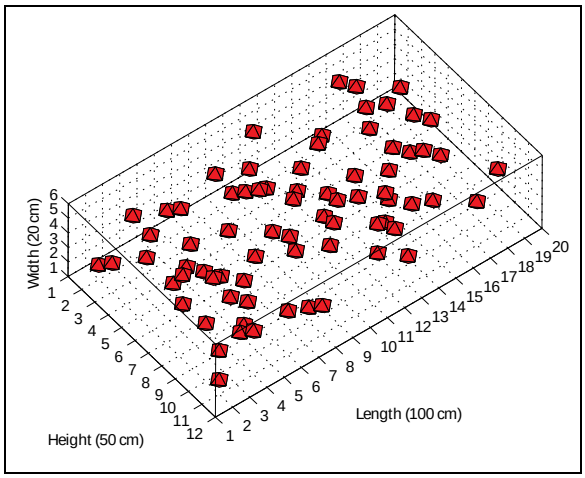


Figure 1: Grid coordinates for placement of spheres inside experimental set-up. Each grid box is equivalent to a 5 cm x 5 cm x 5 cm section of the experimental set-up.

The aluminum box was sealed on 5 sides, with one side (100cm x 20cm) being left open for insertion of the course sand and spheres. A grid was drawn on plastic sheets, which were secured to the interior sides of the box, in order to place the spheres in their appropriate locations. The box was then wet packed layer-by-layer, with external fluorescence probes being inserted from the back of the box as the layers approached their placement zone. A total of 5 probes were inserted approximately 8.5cm inside the column, 85cm from the bottom entrance and 10cm apart. Once the box was filled, the remaining side was sealed shut and the box was set in its upright position. DI water, adjusted to pH 9 using sodium hydroxide, was allowed to run through the box overnight, and then the box was reopened in order to fill in any gaps which occurred due to settling. The box was then allowed to run with pH 9 DI water, in order to ensure no leaking from the box, allow time to calibrate the external flow-through fluorescence probe, set up sampling equipment, and make up the 280 Liters of tracer solution necessary to run the first experiment.

The tracer used for this experimental setup consisted of 1.5 mg/L fluorescein and 25 mg/L Br- (from Lithium Bromide) added to DI water, and adjusted to a pH of 9 using sodium hydroxide solution. 10 Liters of 50x concentrated stock solution was made in order to ensure nearly uniform concentration of the tracer. Tracer solution was made 20 Liters at a time, in order to stay below the maximum capability of the deionized water unit. To each of the 20 Liter containers, 400mL stock solution was added to 19.6 L pH9 DI. This was transferred to a 300 Liter container which was used to store the tracer solution. Once the 280 Liters of tracer solution was mixed, standards were made and analyzed using the flow-through device and the Ocean Optics OOI Base 32 Software. A linear calibration of fluorescein concentration vs. intensity was made, with the intensity of the peak being read at a wavelength of 514.47 nm. Calibrations were also done for bromide and lithium, using the IC and the ICP respectively.

Tracer was then pumped into the bottom of the box at a flow rate of 5 ml/min, with fluorescence data being collected through the flow-through device every 30 minutes and 20 ml aqueous samples being taken with the Gilson 223 sample changer every 24 hours. After 500 hours, the concentrations of all tracer elements had nearly reached their injected concentration,

so further aqueous samples were not taken (Figure 2). The box inlet and outlet lines were valved shut and the box was allowed to equilibrate overnight, allowing time to switch between tracer solution and pH9 DI as the injection fluid. Calibration of the fluorescence device was also performed during this time in order to ensure accurate measurements of concentration vs. time data. Once everything was ready, the pump was started again at 5 ml/min, the valves were opened, and the sampling processes were started again.

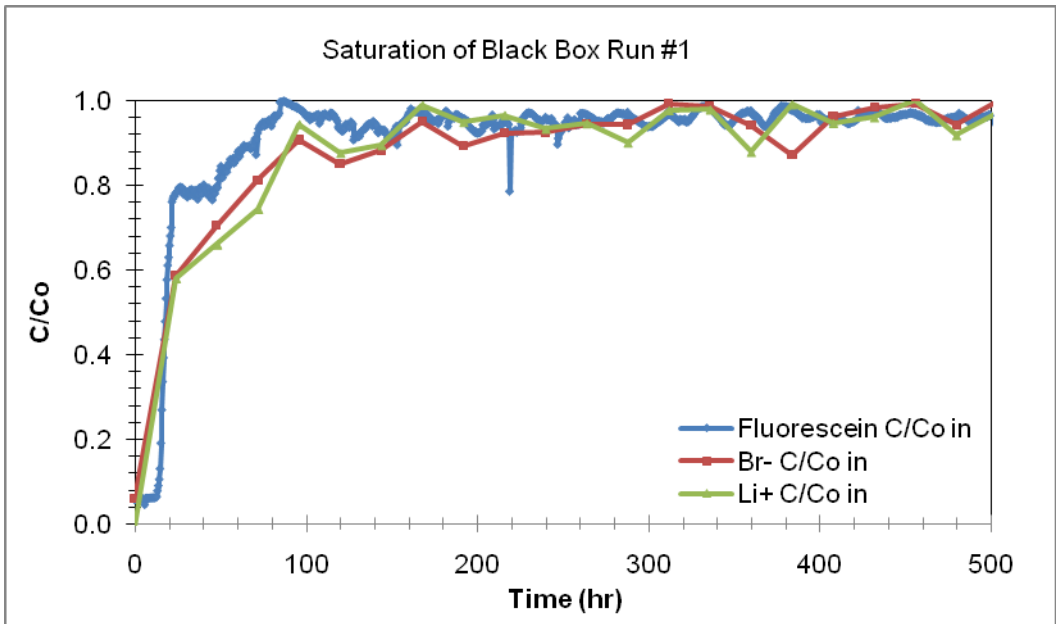


Figure 2: Dimensionless concentration vs. dimensional time data for the saturation portion of the first tracer experiment through the highly heterogeneous experimental 'black box' system. Data shown were taken at the outlet of the box through the use of a flow-through spectrophotometer.

Desaturation of the box took over 1000 hours to complete. In looking at the resultant concentration vs. time data from the desaturation (Figure 3), it is evident that the experimental system does result in non-Fickian tailing. This is evident due to the sharp decrease in concentration followed by a prolonged tailing. Currently a computer model is being constructed, which will be used to describe the experimental results, and a second experimental run is being prepared in order to validate the current results and allow for statistical variations in the concentration vs. time data.

Due to the prolonged timeframe of the experiments being run, testing was done to determine an appropriate antimicrobial additive for the injected water and tracer solution to ensure no unwanted microbial growth within the system. A variety of chemicals were tested, including bleach, EDTA, Triclosan, Thymol, and Zinc Chloride with Sodium Borate. Nearly all tested chemicals impaired the analyses of tracer concentrations in their own way. Bleach neutralized the fluorescence of the fluorescein dye; EDTA reacted with lithium, causing its transport to be retarded; Triclosan and Thymol both increased the peak area for bromide in the IC analysis due to overlapping of peaks, with Thymol also causing a decrease in lithium peak

area on the ICP; Zinc Chloride and Sodium Borate together caused precipitate formation and an increase in fluorescence intensity, while Sodium Borate alone only increased Fluorescein intensity. It was finally decided that Sodium Borate will be used as an antimicrobial agent in all subsequent experiments due to its minimal effect on the tracers used.

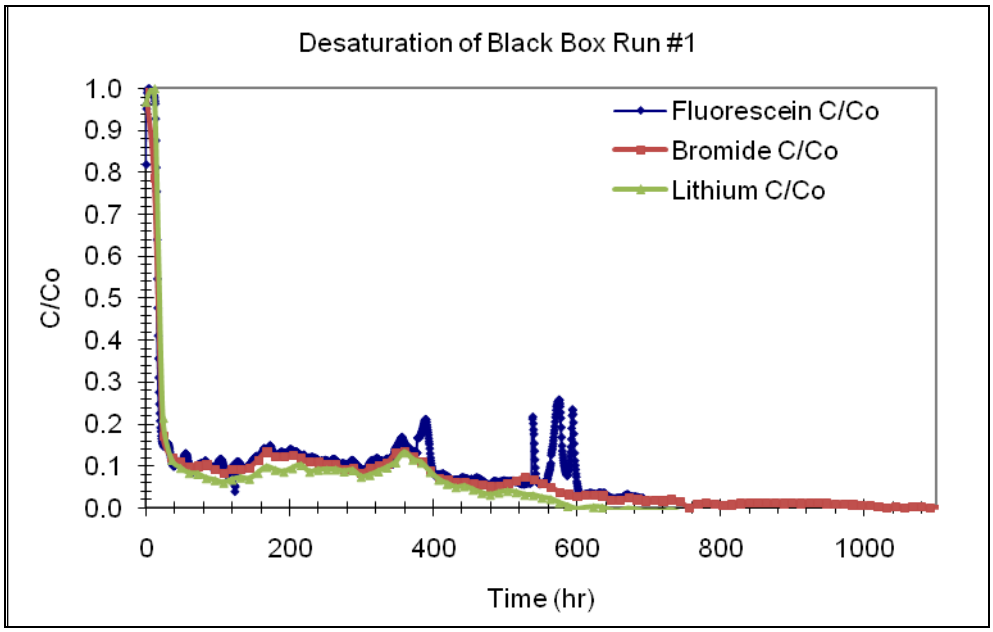


Figure 3: Dimensionless concentration vs. dimensional time data for the desaturation portion of the first tracer experiment through the highly heterogeneous experimental 'black box' system. Data shown were taken at the outlet of the box through the use of a flow-through spectrophotometer.

## FUTURE WORK

Currently, a second experiment is being prepared to validate the initial results obtained in the first tracer experiment, shown above. After validation is complete, internal probes will be calibrated for collection of 3D data during a third tracer experiment. These results will be used to develop a three-dimensional theoretical model for the transport of these solutes in the experimental highly heterogeneous system. The model will be validated through correlations to this research, as well as previous studies. Other experiments are also being planned for this experimental system, including transport of colloids and microorganisms.

## References


1. Berkowitz, B., et al., *Physical pictures of transport in heterogeneous media: Advection-dispersion, random-walk, and fractional derivative formulations.* Water Resources Research, 2002. 38(10): p. 1191, doi:10.1029/2001WR001030.

2. Berkowitz, B., H. Scher, and S.E. Silliman, *Anomalous transport in laboratory-scale, heterogeneous porous media.* Water Resources Research, 2000. 36(1): p. 149-158, paper # 199WR900295.

3. Cherblanc, F., A. Ahmadi, and M. Quintard, *Two-medium description of dispersion in heterogeneous porous media: Calculation of macroscopic properties.* Water Resources Research, 2003. 39(6), 1154, doi:10.1029/2002WR001559.

4. Cushman, J.H. and T.R. Ginn, *Fractional advection-dispersion equation: A classical mass balance with convolution-Fickian flux.* Water Resources Research, 2000. 36(12): p. 3763-3766, paper # 2000WR900261.

5. Deng, F.-W. and J.H. Cushman, *Comparison of moments for classical-, quasi-, and convolution-Fickian dispersion of a conservative tracer.* Water Resources Research, 1995. 31(4): p. 1147-1149, paper # 94WR02853.

6. Haggerty, R., S.A. McKenna, and L.C. Meigs, *On the late-time behavior of tracer test breakthrough curves.* Water Resources Research, 2000. 36(12): p. 3467-3479, paper # 2000WR900214.

7. Meerschaert, M.M., D.A. Benson, and B. Baumer, *Multidimensional advection and fractional dispersion.* Phys. Rev. E., 1999. 59(5): p. 5026-5028.

8. Quintard, M., F. Cherblanc, and S. Whitaker, *Dispersion in heterogeneous porous media: One-equation non-equilibrium model.* Transport in Porous Media, 2001. 44: p. 181-203.

9. Wood, B.D., et al. *Upscaling Transport in Two-region Bimodal Porous Media: Comparison of Theory and Experiment.* In *Proceedings of the SIAM Conference of Mathematics and Computational Issues in the Geosciences (GS03)*. 2003a. Austin, Texas: Society for Industrial and Applied Mathematics.

10. Zhang, Q., *Multi-length-scale theories for scale-up problem and renormalized perturbation expansion.* Advances in Water Resources, 1997. 20(5-6): p. 317-333.

11. Zinn, B. and C.F. Harvey, *When good statistical models of aquifer heterogeneity go bad: A comparison of flow, dispersion, and mass transfer in connected and*

***multivariate Gaussian hydraulic conductivity fields.*** **Water Resources Research, 2003. 39(3), 1051, doi:10.1029/2001WR001146.**